

MARKSCHEME

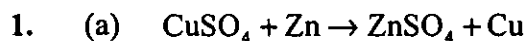
November 1999

CHEMISTRY

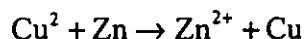
Higher Level

Paper 2

SECTION A



OR



[1]

States not necessary to gain mark

(b) $\left. \begin{aligned} \text{Amount of Zn} &= \frac{1.20}{65.37} = 0.018 \text{ moles} \\ \text{Amount of Cu}^{2+} &= \frac{50}{1000} \times 0.200 = 0.010 \text{ moles} \end{aligned} \right\}$

[1]

therefore Zn is in excess

[1]

- (c) At point A the heat being given out by the reaction is equal to the heat being lost to the surroundings.

[1]

Do not give the mark for "the reaction is finished".

- (d) Correct extrapolation to when the zinc was added.

[1]

Give no marks if the line is extrapolated to the Y axis.

Temperature rise = $26.7 - 17.0 = 9.7^\circ \text{C}$

[1]

Accept $26.7 \pm 0.1^\circ \text{C}$ giving 9.6 to 9.8°C

(e) Heat = $9.7 \times 4.18 \times 50$ Give credit if 51.2 g taken as mass [1]
 = 2027.3 J = 2030 J Answer must be given to 3 sig. figs. to gain mark [1]

Consequential markings from (d)

(f) $\Delta H = -2030 \times 100 \text{ J}$
 = -203 kJ mol^{-1}

[1]

(g) Error = $\frac{218 - 203}{218} \times 100 = 6.9 \%$

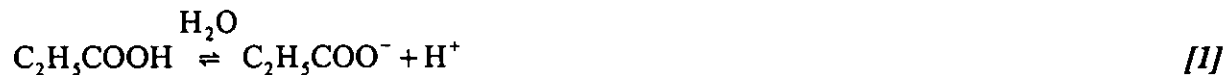
[1]

- (h) [1 mark] each for any two valid reasons

e.g. not carried out under standard conditions;
 heat loss as polystyrene beaker did not act as an adequate insulator;
 solution assumed to have same specific heat capacity as 50 g of water;
 Heating of metal (Cu + excess Zn), thermometer etc. ignored.

[2]

2. (a) $\text{C}_2\text{H}_5\text{COOH} + \text{H}_2\text{O} \rightleftharpoons \text{C}_2\text{H}_5\text{COO}^- + \text{H}_3\text{O}^+$
OR



(b) $K_a = \frac{[\text{C}_2\text{H}_5\text{COO}^-][\text{H}^+]}{[\text{C}_2\text{H}_5\text{COOH}]} \quad [1]$

(c) $\text{p}K_a = 4.87$ therefore $K_a = 1.35 \times 10^{-5}$
Therefore $1.35 \times 10^{-5} = \frac{[\text{H}^+]}{[\text{C}_2\text{H}_5\text{COOH}]} = \frac{[\text{H}^+]^2}{0.200} \quad [1]$

Therefore $[\text{H}^+] = \sqrt{2.70 \times 10^{-6}}$ therefore $[\text{H}^+] = 1.64 \times 10^{-3}$
Therefore $\text{pH} = 2.78 \quad [1]$

OR

$$10^{-4.87} = \frac{[\text{H}^+]^2}{0.200} \quad (11)$$

Therefore $4.87 = 2\text{pH} + \log_{10} 0.200$

Therefore $2\text{pH} = 4.87 + 0.699$

Therefore $\text{pH} = 2.78 \quad (11)$

Have assumed $[\text{C}_2\text{H}_5\text{COOH}]_{\text{eqm}}$ is $0.200 \text{ mol dm}^{-3}$ or $[\text{H}^+] \ll [\text{C}_2\text{H}_5\text{COOH}] \quad [1]$

- (d) When $[\text{C}_2\text{H}_5\text{COO}^-] = [\text{C}_2\text{H}_5\text{COOH}]$

$\text{p}K_a = \text{pH} = 4.87$

Therefore $[\text{C}_2\text{H}_5\text{COO}^-] = 0.200$

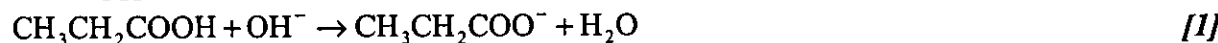
Therefore $0.100 \text{ mols of NaCH}_3\text{CH}_2\text{COO in } 500 \text{ cm}^3$

Therefore $\text{mass} = 0.100 \times [22.99 + 36.03 + 32.00 + 5.05]$
 $= 9.61 \text{ g} \quad [2]$

- (e) When H^+ is added it combines with $\text{CH}_3\text{CH}_2\text{COO}^-$ to form the acid.



When OH^- is added it reacts with the acid to form water.



3. (a) Zinc does not have a partially filled d sub-level in any of its oxidation states.
(must include something about oxidation states or compounds) [1]
- (b) $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5$ accept $[Ar] 3d^5$ [1]
- (c) e.g. V (+4, +5) or Cr (+3, +6) or Mn (+4, +7) [1]

or any other correct answer

both oxidation states must be correct for the mark

- (d) Formula: $[Fe(H_2O)_6]^{3+}$ [1]

Octahedral or diagram [1]

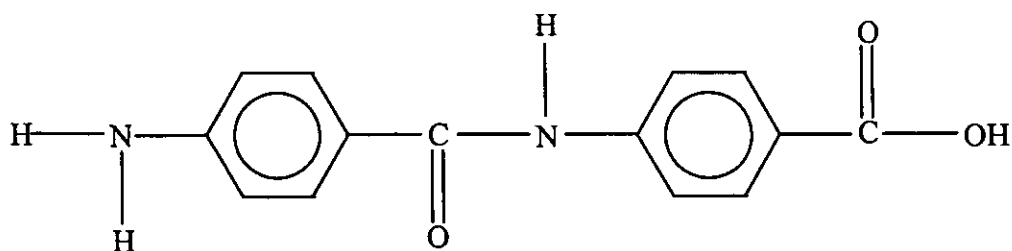
- (e) Sc^{3+} does not have a partially filled d sub-level. [1]

The colour of Fe^{3+} is due to transitions between the d orbitals (which are split by the ligands). [1]

- (f) Iron is added as a catalyst. [1]
To increase the surface area which makes it a more efficient catalyst. [1]

4. (a) Amino group / amine and alkanoic acid/carboxylic acid group. [2]

- (b) (i)



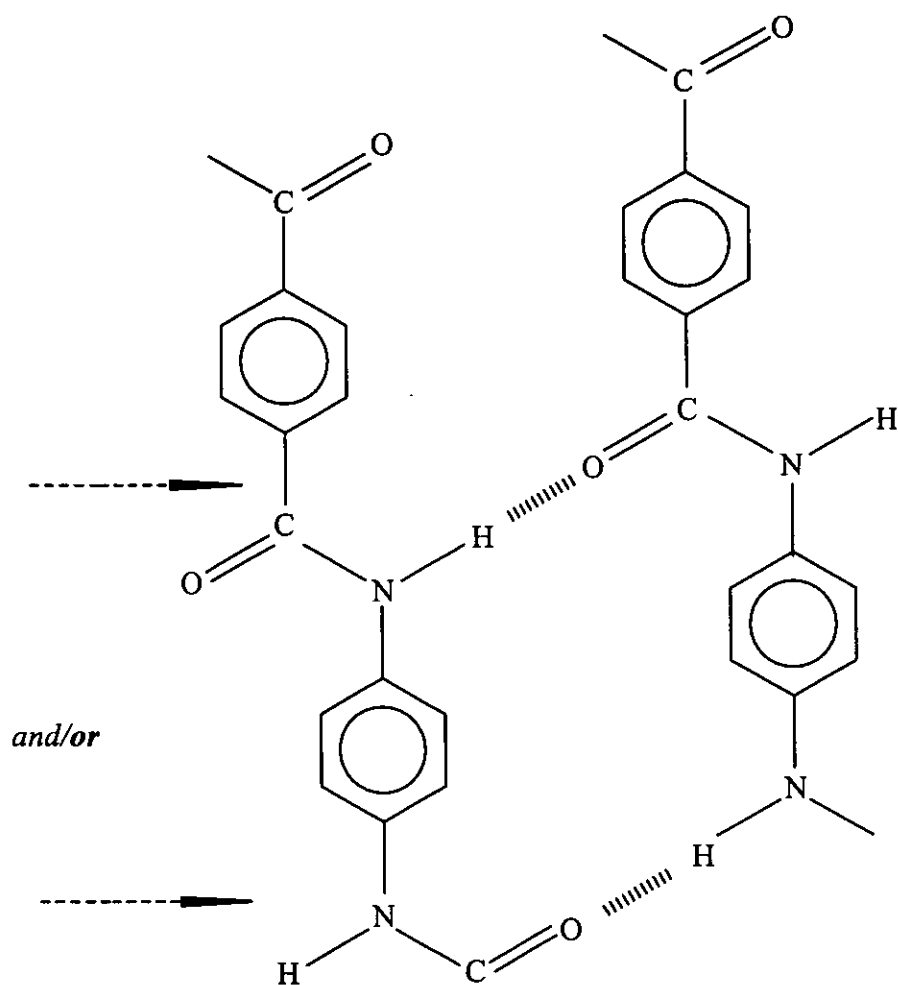
[1]

- (ii) peptide bond accept amide [1]

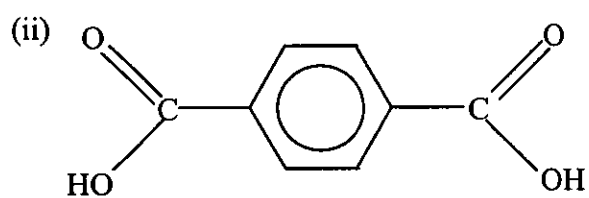
- (iii) water/ H_2O [1]

- (iv) condensation polymerisation/addition-elimination [1]

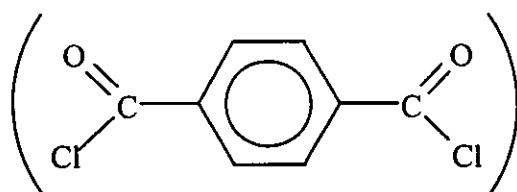
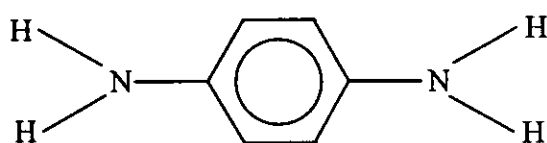
(c) (i)



[1]



or and



[2]

(iii) Benzene rings are planar (flat) or the strands are kept flat by H-bonds.
(accept either)

[1]

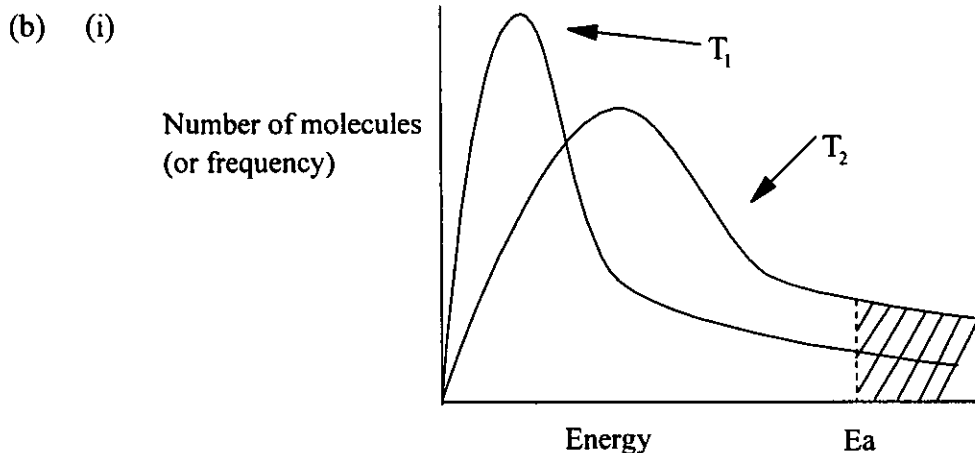
SECTION B

5. (a) (i) A system exhibits dynamic equilibrium when the **two opposing processes** are proceeding at **equal rates** (*i.e.* the rate of the forward reaction is equal to the rate of the reverse reaction). [2]
- (ii) In homogeneous equilibrium **all the reactants and products** are in the **same phase**. [2]
- (iii) A closed system is one in which there is **no exchange of matter or energy** between the system and its **surroundings**. [2]
- (b) $K_c = \frac{[\text{NH}_3]^2}{[\text{H}_2]^3[\text{N}_2]}$ [1]
- Units are: $\text{mol}^{-2} \text{dm}^6$ [1]
- (c) (i) Increasing the volume has no effect on K_c for **both** reactions [1]
as K_c is independent of concentration. [1]
It will not affect the position of equilibrium of the HI reaction [1]
as there is no overall volume change (2 vols → 2 vols). [1]
It will shift the position of equilibrium for the NH_3 reaction to the left (*i.e.* lower the equilibrium concentration of NH_3 relative to N_2 and H_2) [1]
as 4 vols of reactants give 2 vols of products. [1]
- (ii) Lowering the temperature will move the position of equilibrium for the HI reaction to the left (more H_2 and I_2 in the equilibrium mixture) [1]
as the forward reaction is endothermic (heat absorbed) [1]
for the same reason K_c will decrease at lower temperatures [1]
Lowering the temperature will move the position of equilibrium for the NH_3 reaction to the right (more NH_3 in equilibrium mixture) [1]
because the forward reaction is exothermic (heat evolved) [1]
for the same reason K_c will increase at lower temperatures [1]
- (iii) No effect on position of equilibrium [1]
Speeds up both forward and reverse reactions [1]
Does not change K_c [1]
- (d) $\sqrt{\frac{1}{K_c}}$ [1]
- $= \sqrt{\frac{1}{54.7}} = 0.135$ [1]

6. (a) (i) The rate constant is the constant of proportionality relating the rate of the reaction with the (reactants) as they appear in the rate expression. [2]

The activation energy is the minimum energy which the reactants must possess before a collision will result in a reaction. [2]

- (ii) rate: $\text{mol dm}^{-3} \text{s}^{-1}$ [1]
 k : $\text{mol}^{-1} \text{dm}^3 \text{s}^{-1}$ [1]



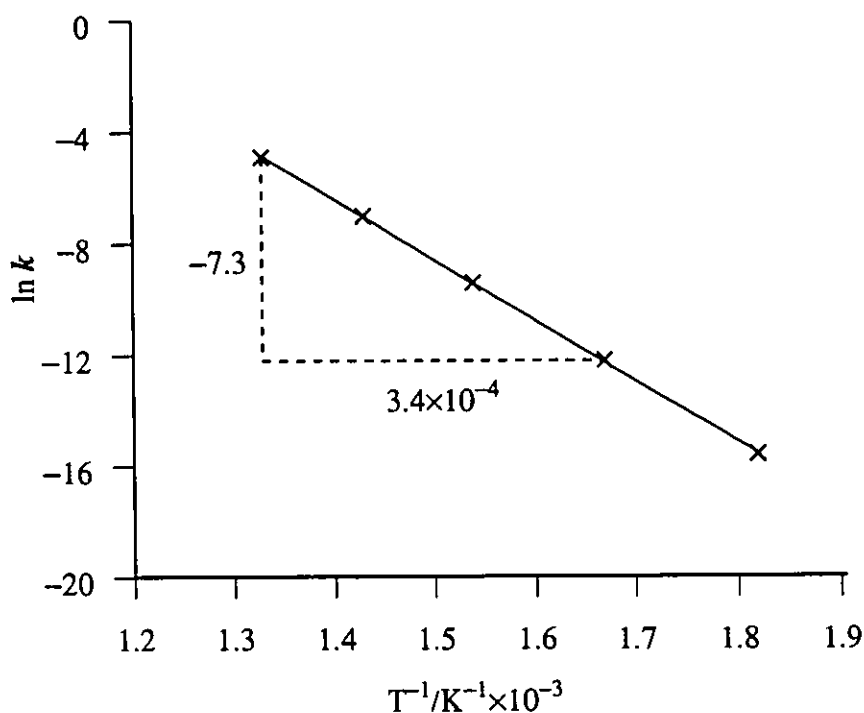
[2 marks] for showing the correct Maxwell-Boltzmann curves with axes labelled.

[2 marks] for curves correctly labelled T_1 and T_2 . [4]

- (ii) An increase in temperature increases the fraction of molecules that possess the necessary E_a . [1]
 Showing E_a correctly on the graph. [1]

- (iii) A catalyst provides an alternative reaction pathway with a lower E_a so that more of the reactant molecules possess the necessary energy to react. [2]

- (c) (i) A correct plot of the data [2 marks] showing negative gradient, labelled axes in the correct range and a straight line [2 marks] (see below). [4]



- (ii) From the graph, gradient = $-\frac{7.3}{3.4 \times 10^{-4}} = -2.15 \times 10^4 \text{ K}$ (accept -2.0 to -2.4×10^4) [2]

if minus sign missing or 10^4 factor missing, then [1 mark]

$$\text{Gradient} = -\frac{E_a}{R} \quad [1]$$

$$E_a = 8.314 \times 2.15 \times 10^4 = 1.79 \times 10^5 \text{ J mol}^{-1} \quad [1]$$

$$= 179 \quad \text{numerical answer}$$

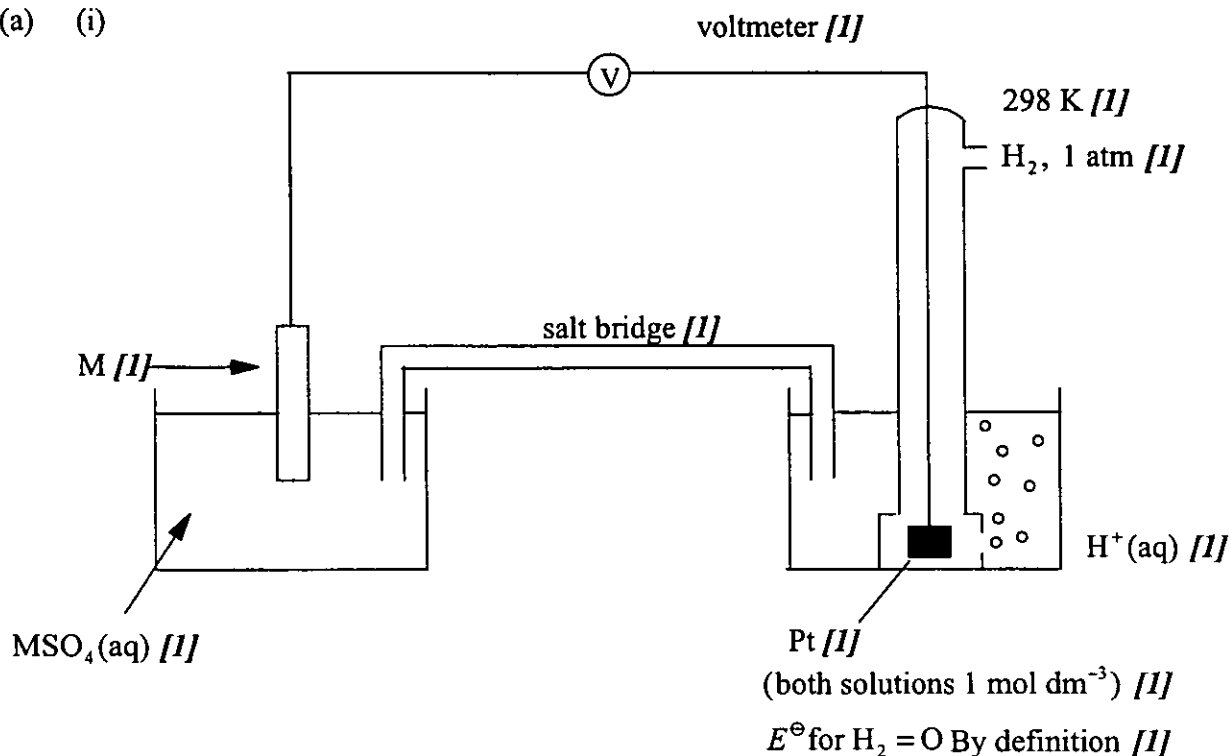
$$\text{(accept 166–200)} \quad [1]$$

$$\text{kJ mol}^{-1} \quad \text{correct units}$$

- (iii) The graph can be extrapolated back to the y axis when $T^{-1} = 0$ to give a value for $\ln A$ and hence A . [1]

Particular values for $\ln k$, T^{-1} , E_a and R can be put in the Arrhenius equation to give a value for $\ln A$ and hence A . [1]

7. (a) (i)



OR description in words

[1 mark] each for any 8 correct.

[8]

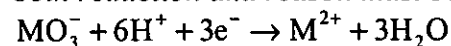
(ii) +5

[1]

Reduction because there is a gain of electrons (or a decrease in oxidation number).

[1]

both reduction and reason must be stated for mark



[1]

(iii) E^\ominus is higher for $\text{MO}_3^- / \text{M}^{2+}$ than for $\text{Br}_2 / \text{Br}^-$ (+1.09 V from Data Booklet).

[1]

Therefore MO_3^- must be a more powerful oxidant than Br_2 .

[1]

Therefore MO_3^- will oxidise Br^- to Br_2 .

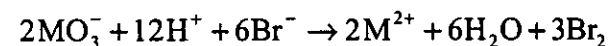
[1]

OR

For a reaction to occur E_{cell} must be positive.

For the reaction between MO_3^- and Br^- E_{cell} is +0.11 V.

Therefore this reaction can take place.



[1]

Mix aqueous solutions containing (1 mol dm⁻³) MO_3^- and Br^- .

[1]

Positive result – solution turns yellow/orange brown.

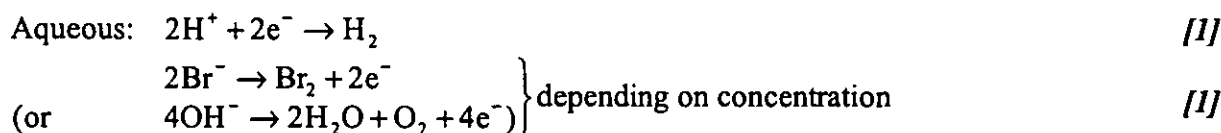
[1]

Negative result – solution remains colourless.

[1]

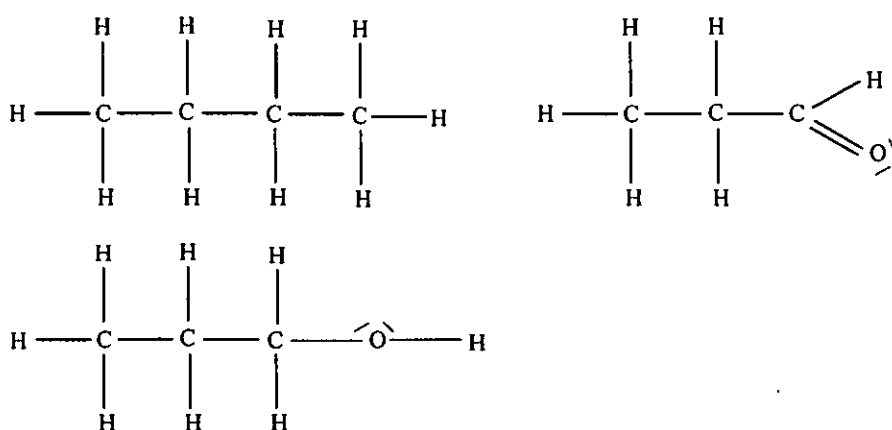
If the E_a is high the reaction may not occur/may be very slow.

[1]



In aqueous solution H^+ is discharged as it is easier to reduce (more positive E^\ominus or lower in electrochemical series) than K^+ . In molten KBr there is only one cation present. [2]

8. (a) (i)



[1 mark] for each structure, accept dot and cross diagrams but **all** outer electrons must be shown whichever method is used. [3]

If the non-bonding electron pairs are not shown for propanal, do not award mark. However, do not penalise twice if they are also not shown for propan-1-ol.

- (ii) butane: all four carbon atoms are sp^3 hybridised [1]
 propanal: two sp^3 and one sp^2 [1]
 propan-1-ol: all three are sp^3 hybridised. [1]

(b) $\hat{H}OC$ in propan-1-ol is just less than 109° [1]

accept $104^\circ - 108^\circ$ but **not** 109° or greater.

$\hat{H}CO$ in propanal is approximately 120° [1]

- (c) (i) Butane is a **non polar molecule** so the attractive forces between butane molecules are only relatively **weak van de Waals** attractions. [2]
 (ii) Propan-1-ol contains H joined directly to the very **electronegative O atom** which results in **strong H-bonding** between molecules of propan-1-ol. [2]
 (iii) **Oxygen is more electronegative than carbon** so the bond between them will be polar resulting in **dipole:dipole** attractions between propanal molecules. [2]

- (d) Can be explained **either** in terms of the negative ion formed:
In the RO^- ion the negative charge is localised on the O atom so there is a high negative charge density, so the ion will strongly attract an H^+ ion and return to the undissociated alcohol. In the carboxylate ion the negative charge is delocalised (*accept resonance hybrid explanation*) over the C atom and the two O atoms so the charge density is considerably reduced, decreasing the attraction of the ion for H^+ .

OR

The carbonyl O withdraws electrons from the C due to its high electronegativity. The carbon in turn withdraws electrons from the hydroxyl O weakening the O-H bond in propanoic acid.

[3]

- (e) Any **three** from:
All the C-C bond lengths are equal.
All the C-C bond enthalpies are equal.
Benzene does not readily undergo addition reactions.
Two isomers of 1,2-disubstituted benzene compounds do not exist.
The enthalpy of hydrogenation or combustion of benzene is not equal to the value expected for three separate double bonds.
The ^1H NMR shift for benzene is very different to an alkane or alkene.
The ^1H NMR spectrum for benzene shows only one peak.

[3]

or any other valid piece of evidence

All the C atoms are sp^2 hybridised. The remaining six electrons (one from a p orbital on each C atom) form a delocalised π bond over all six C atoms. This results in a planar molecule with a volume of electron density due to the delocalised π bond above and below the ring.

OR

accept a well-explained diagram

[2]

The formation of the delocalised π bond results in extra stability for the molecule (approximately 150 kJ mol^{-1}). This explains why it does not readily undergo addition reactions (extra energy would be required to overcome the delocalised π bond) and why the enthalpy of hydrogenation and combustion is less than expected. Since all the C-C bonds are equal (in between a C-C and C=C bond) all bond lengths and strengths will be the same and there cannot be two isomers for 1,2-disubstituted benzene compounds.

[3]

[1 mark] for each matching up correct explanation with each of the three reasons given above.